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Specification and Drawings, as originally filed, with Application for Patent Serial No:
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"Method of Picking the Electrolyte for High Capacity Electric Energy Accumulators".

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METHOD OF PICKING THE ELECTROLYTE FOR HIGH CAPACITY ELECTRIC ENERGY ACCUMULATORS

The novelty and distinctiveness of this method for picking the electrolyte is based on the distinctiveness of EMONA from other traditional electrolytic capacitors of double layer (KDC) and subsequently, due to principally different conditions of its work.

Description of the Work Conditions

Traditional electrolytic KDC, representing a pair of metal electrodes, one of which is covered by a dielectric film (for example, the anode film formed as a result of the chemical effect on the surface of the electrode) which does not allow the passage of the electrolyte to the metal surface. A membrane is placed between the electrode (as a rule, it is of a fibrous structure) saturated with the electrolyte. Such membrane performs the function of the electrolyte carrier. The electrodes-metal and metal covered with the dielectric film are inert in relation to the electrolyte provided that the conditions of their work are preserved (polarity, voltage).

The EMONA is a device, consisting of at least one, more often of several, cells, divided between themselves and from the current collectors by chemically inert conducting non-transparent for the electrolyte particle separators; each of such cells includes in itself a couple of electrodes consisting of one or several layers of chemically inert carbonised activated conducting fibrous material which has a developed surface, active centres and orderly structure; the electrode pair is divided within itself by a chemically inert non-conducting transparent for the electrolyte particles membrane. This device is enclosed in an air-tight body.

The electrolyte that is used is a liquid substance (clear liquid, liquid mixture, solution, gel, etc.) in which the electrodes and the chemically inert non-conducting transparent for the electrolyte particles membrane are saturated.

The electrolyte is usually found in the adsorbed form in the material of the electrodes and the membrane, while free volume of the electrolyte is absent.

The electrolyte is in direct contact with the chemically inert conducting surface of both electrodes.

Each cell of EMONA is originally symmetrical in relation to the chemically inert non-conducting transparent for the electrolyte particles membrane.

Theoretical Basis

The use in the EMONA of the above described construction of the cell and materials requires the development of a special method for choosing the electrolyte. Processes leading to the charging of the device (accumulation of the electric energy) and processes for its use in the electric chains (output of the stored energy) are substantially different from the processes taking place in the traditional chemical sources of current in electric KDC with the metallic electrodes, despite the fact that they do not go beyond the laws of saving the charge and energy.

For your comparison we will provide fragments of charged capacitors: that of the electric KDC with the metallic electrodes and that for EMONA.

Scheme 1 represents a fragment in which:

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- 1 - the metallic electrodes (for example A1);
 - 2 - the anode oxidizing layer - dielectric with the thickness d and dielectric constant $E > 2$;
 - 3 - porous membrane saturated with dry electrolyte. Generally, the electrolyte is a highly viscous liquid containing polar molecules.

When charging the capacitor, the applied electric field influences the polar molecules of the electrolyte so as to orientate their polarization as it is shown on the

scheme. In turn, the oriented molecules of the electrolyte cause the induced polarization of the molecules of the hard dielectric. As a result, the creation of the polarized charges of the dielectric in the electrolyte lead to the redistribution of the concentration in the metal "electron gas": on the anode - n_1 , on the cathode - n_2 , provided that $n \geq n_1$. Therefore, the role of the electrolyte is limited to that of creating the polarized charges during the capacitor charging. The electro-capacity of the capacitor is defined only the thickness of the dielectric layer and its dielectric constant. The working voltage of the capacitor is in complete dependence from the qualities of the dielectric layer and the concentration of the conduction electrons, appearing in the inter-electrode space because of the "autoelectronic emission" of the electrons.

According to the Fermi-Dirak statistics, such electrons always are present when the temperature is $T > 0K$. When the capacitor is charged, additional favourable conditions are created which allow the increase in their concentration (when the value of d voltage of the electric field near the internal borders of metal can reach 10^4 - 10^5 V/cm, therefore the electrolytic metal capacitors have large "leakage currents".

When the voltage is increased, the dielectric breakdown takes place, at which time the electrolyte is decomposed and huge amounts of gas are emitted. These changes lead to the capacitor getting out of order. Such changes do not allow the use of such capacitors in the chain of alternating current, or at the polarity reversal.

Therefore, one can use as the working voltage, voltage during which no breakdown of the dielectric layer takes place.

When analysing the analogous fragment of the charged EMONA device, we proceed from the available experimental results, absence of a certain polarity at the initial stage and the possibility of the polarity reversal after the charge; as a result of this, the possibility of using in the chain of alternate current; furthermore, multiple experiments show that in the fibrous structures, under complicated conditions, many qualities of the liquids (broadcasting diffusion, viscosity, temperature of boiling and hardening, the

coefficient of refraction and others) change considerably. The analysis of the structure of carbonised activated material by means of electronic microscopy, Auger spectroscopy, and others lead to the qualitative representation of its character: availability of two types of pores - micro-pores - size about $(5-10) \times 10^{-10} \text{m}$ and macro-pores - size approximately $100 \times 10^{-10} \text{m}$ and more; distribution according to the size is impossible to define. At the same time, the process of carbonisation, according to the generally accepted view, and graphitization of the materials possible at the so called sp^2 - hybridization of the carbon valence electrons. In other words, the energetic state of the valence electrons is changed.

Scheme 2 represents a fragment of the charged EMONA in the simplified version (ideal variant), when at the time of charging a complete separation of positive and negative charges took place (for simplification, the charges are represented without the accompanying hydrate and solvate shells). Since the "electronic gas" is absent in the carbon graphitized structures, such picture is possible only provided that the redistribution (deformation) of the electronic density of the surface or the transformation of the energetic condition of the carbon valence electrons. This phenomena reminds of the electronic polarization in the non-polar dielectrics. However, the graphitized carbon structures act as transmitting media and, therefore, it is possible to assume the availability of an "exchange" mechanism of their conductance.

In any case, the changes in the electron density of the carbon surface must be compensated by the change in the concentration of the "electron gas" in the metallic current collectors, that is, similar to the metallic electrodes in the electrolytic KDC, they must contain both n_1 (similar to the anode) and n_2 (similar to the cathode), and $n_2 > n_1$.

This picture allows us to explain all phenomena observed during the use of a device in the chain of constant and alternative current. Therefore, in this situation the role of the electrolyte is different than in the case of the electrolytic KDC.

During the charge, a double electric layer is formatted immediately on the surface of the electrode, and it certain structuralization takes place. At the same time the structure

that is deeper in its layer, simultaneously with the formation of the charge, creates a certain screening shield of the charges, located immediately at the surface of the material. From this picture it is possible to define the conditions necessary for the successful work of the capacitor. Since the redistribution of the charges takes place under the influence of the electric field, the maximum possible voltage will be such that does not allow the charges' discharge at the surface of the material. When the voltage is higher than allowed, the charges at the surface will be discharged, and this will result in their neutralization. Since the charges closest to the surface start discharging first of all, once having discharged, they would decrease the area of the layer (partially screened shielded from further located charged layers). If one studying the characteristics of the capacitor at this stage, at these and higher levels of voltage, these characteristics would have to change. Our experience indicates that such changes do not reflect considerably on the capacity, yet the current of short circuit changes more drastically.

It does not seem possible to define the voltage corresponding to the beginning of the electrolyte disintegration (the discharge of the charged particles at the surface of the electrode). For example, when the gas-forming carriers of the charge are discharged, the gas may be formed, or not, depending on the surface density of such charges in the layer closest to the porous carbon surface based on the above described.

The above-noted reveals how the method of choosing the electrolyte and its working voltage for EMONA is defined.

Description of the Method

This method involves the following:

(a) Taking Measurements

- One must measure the volt-ampere characteristics of the elementary EMONA cells with the electrolyte being tested on the short circuit current:

$$I_{sc} = f(U).$$

- Every time EMONA is charged to a certain voltage value U_i (generally, starting from 0 volt with a certain step, provided that $U_i > U_{i-1}$). When the value of the charging coefficient is identical, for example, $K_{ch} = 1.03$, which represents the correlation between the voltage on EMONA at charging to the voltage remaining on EMONA after its disconnection from the charging device.
- The current of the short circuit is defined in the EMONA, charged this way and when disconnected from the charging device, for example with the help of the Oscillograph and the calibrated shunt.
- The volt-ampere characteristic received in this way looks the same for any kind of electrolyte (we have examined more than 40 different types of electrolyte), and is reflected on scheme No. 3 (curve O-e₁).
- Particularly, the characteristic received for 1N water solution of the sulphuric acid revealed disintegration voltage of 1.6-1.7 volt, which coincides with the well-known for the disintegration voltage of such electrolyte 1.67 volt.

(b) Received Data Analysis

- From the analysis of the volt-ampere characteristic, one defines the point from which the angle of the curve starts to decrease, that is

$$\frac{d}{du} \left(\frac{dI}{dU} \right)$$

changes its mark to the negative (m on Scheme No. 3). Voltage corresponding to the found point will indicate the voltage corresponding to the beginning of the electrolyte disintegration.

- At the same time

$$\frac{dU}{dI}$$

is increasing. This can be called the internal resistance. With further increase in the internal resistance voltage, the short circuit current reaches its maximum and starts to decrease.

- Such increase and the internal resistance growth is irreversible. If one had to measure, after the discharge, this characteristic (curve $O-e_2$) at its initial point, it would correspond to the highest internal resistance of the previous cycle coincides with curve $O-e_1$). The polarity of the first and the following charge-discharge cycle does not influence the voltage corresponding at the beginning of the characteristic bending.

(c) Choosing the Range of the Working Voltages

- The disintegration voltage found this way will represent the maximum possible voltage for such electrolyte in the conditions of EMONA, U_{max} . When EMONA is used, this electrolyte is fit to work at the level of charge voltage not higher than U_{max} irrespective of the polarity.

- In order to increase the reliability of the electrolyte work within EMONA, one should accept as the nominal working voltage U_{nom} voltage a little bit lower than the maximum allowed. One would include the coefficient of supply K_u (usually 1.2-1.4), that is $U_{nom} = U_{max}/K_u$.

- Therefore, the working voltage U_{work} for this electrolyte can be any voltage value of which does not exceed U_{nom} (section of the characteristic $O-N$ on Scheme No. 3). The working voltage selected this way must provide the guaranteed device power.

- During the work within the parameters of this range (a shaded part of Scheme No. 3) one would provide stable parameters of EMONA and theoretically unlimited number of large discharge cycles, as well as the longevity of work, including, when plugging into the chain of pulsating or alternating current (one should remember that EMONA, as other traditional capacitors, is charged to the peak value of voltage).

Scheme No. 1 - Segment of the Charged Electrolytic KDC

- (a) Metallic electrodes.
- (b) De-electric (oxidized layer).
- (c) Porous membrane saturated with "dry" electrolyte.

Scheme No. 2 - Segment of the Charged EMONA Elementary Cell, Simplified Model

- (a) Current collectors (metal).
- (b) Inert conducting non-transparent for the electrolyte separators.
- (c) Electrodes made of the carbonised activated conducting fibrous material of orderly structure.
- (d) Non conducting transparent for the electrolyte membrane.

Scheme No. 3 - Volt-ampere**Characteristic of EMONA**Formula of the Invention

1. The suggested method is based on the definition of the working capacity of certain electrolyte in the conditions of EMONA on the basis of analysing the received volt-ampere characteristic, and is expressed in the following:
 - 1.1 One must measure the volt-ampere characteristic of the EMONA sample with the electrolyte being tested.
 - 1.2 One must define the point on the characteristic which corresponds to the voltage at the time of exceeding which

$$\frac{d}{dU} \left(\frac{dI}{dU} \right)$$

becomes less than 0.

- 1.3 Voltage corresponding to the point found according to 1.2 is considered the maximum allowed for such electrolyte within the conditions of EMONA.
 - 1.4 The measurements under 1.1 are conducted on an elementary cell.
 - 1.5 The characteristic under 1.1 is measured on the short circuit current.
 - 1.6 The characteristic under 1.1 is measured beginning with 0V, with a certain step, to the voltage where each following voltage is higher than the previous one.
 - 1.7 One considers as the nominal voltage, voltage slightly less than that in 1.3, the coefficient of storage for the voltage $K_u = U_{\max}/U_{\text{nom}}$.
 - 1.8 The working voltage applied to one EMONA cell does not exceed the one under 1.3 or 1.7.
2. The method under 1. defines the allowed working regimes for any device which work according to the principles similar to those in EMONA.
 3. The method under 1. defines the discharge voltage for any liquid substance (pure liquid, solution, melt, condensate, gel, ash and their mixtures).
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Рис. 1
Качественные характеристики ЕМОНА

а). Типичная зарядная характеристика

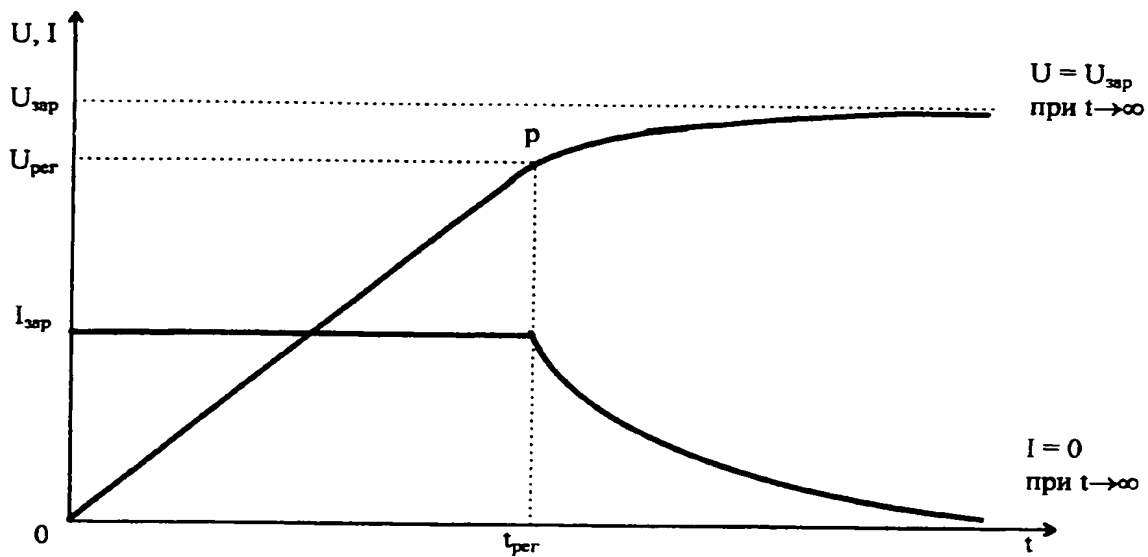


Fig. 1

б). Типичная разрядная характеристика

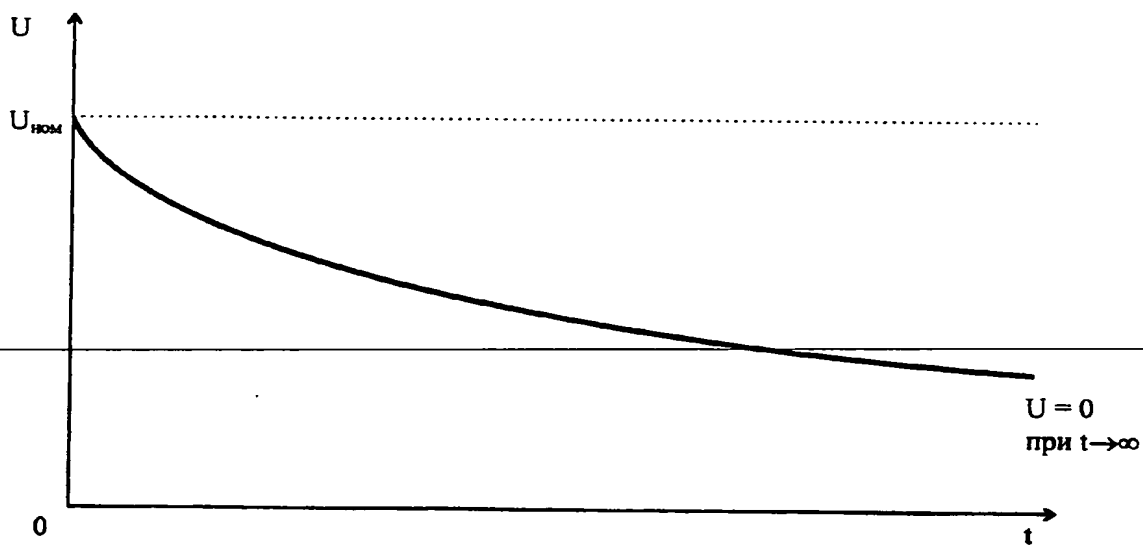


Fig. 2

Рис. 2
Качественные характеристики ХИТа

а). Типичная зарядная характеристика

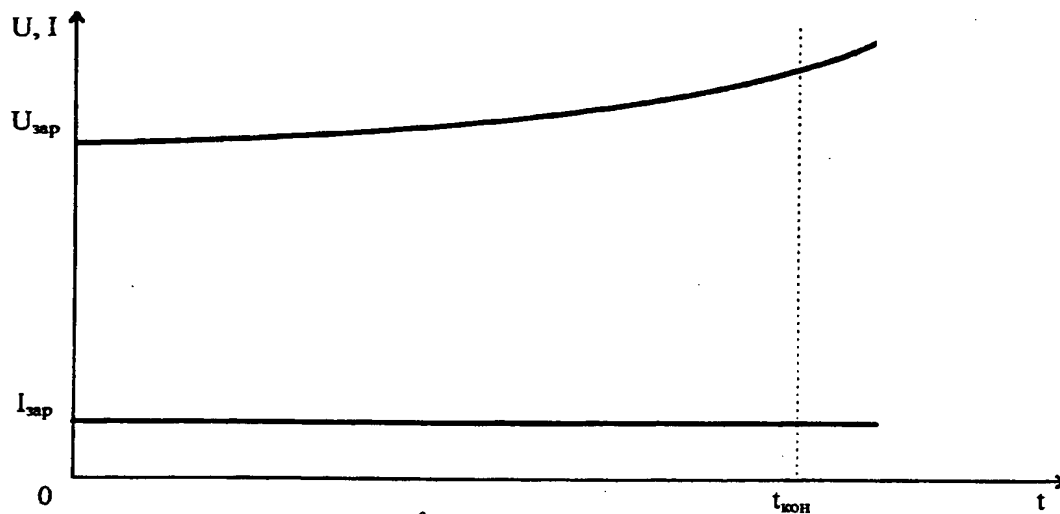


FIG. 3

б). Типичная разрядная характеристика

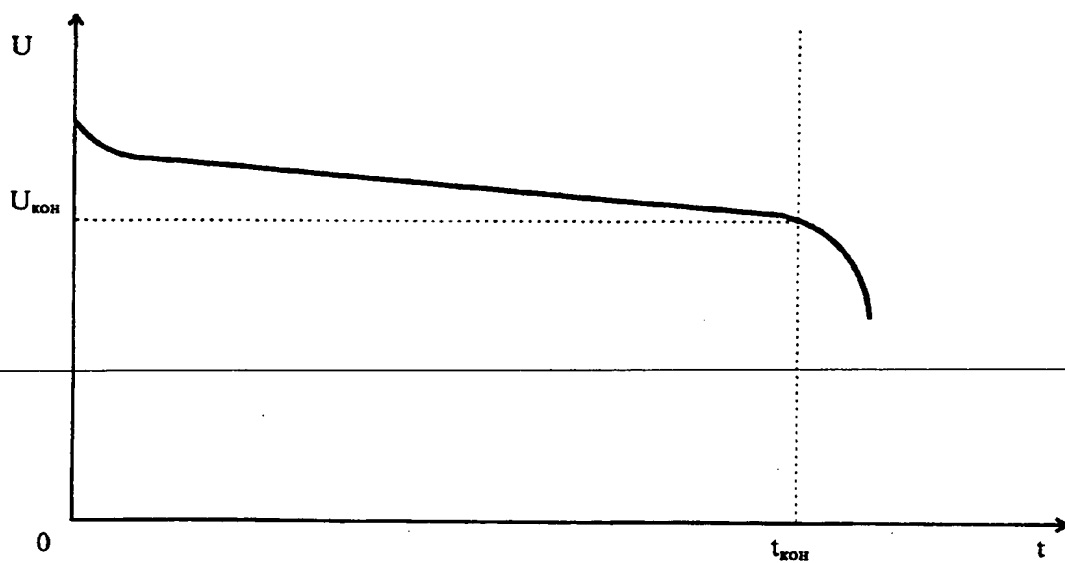


FIG. 4

Рис. 3
Разрядная характеристика батарей из двух модулей ЕМОНА с использованием переключения между модулями с параллельного на последовательное

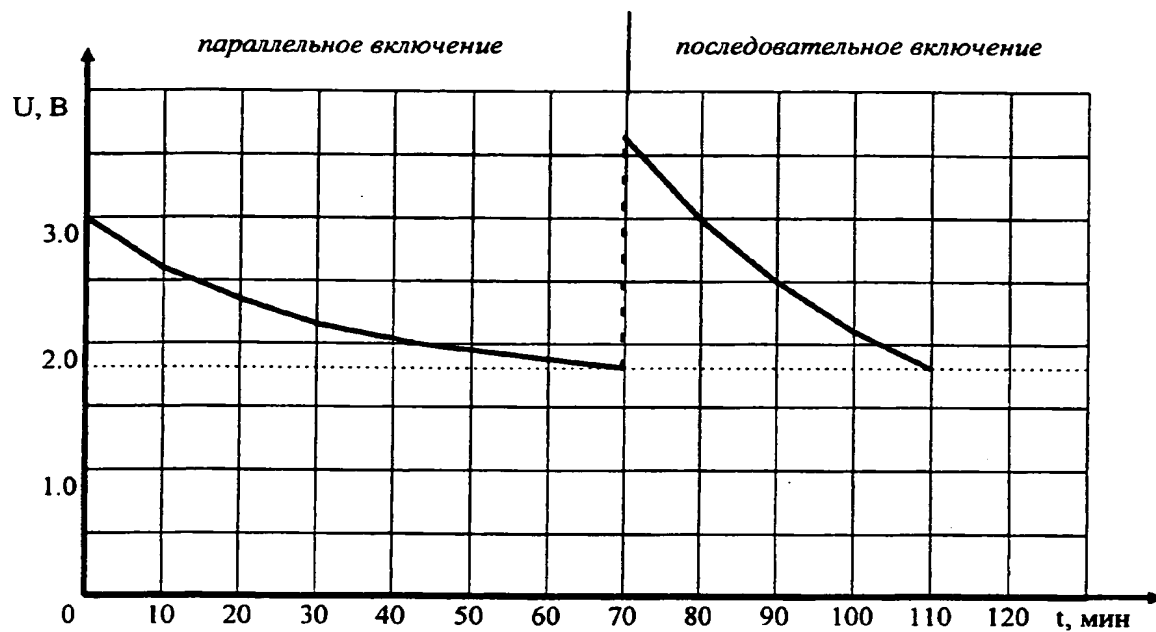


Fig. 5

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